

The University of Chicago

THE PREPARATION OF
DEUTOHYDROGEN BY ELECTROLYSIS
AND BY ACTION OF METALS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1934

By
CLINTON M. DOEDE

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1937

The University of Chicago

THE PREPARATION OF
DEUTOHYDROGEN BY ELECTROLYSIS
AND BY ACTION OF METALS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1934

By
CLINTON M. DOEDE

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS
1937



ACKNOWLEDGMENT

The writer wishes to express his sincere appreciation to Dr. W. D. Harkins for the suggestions and helpful guidance given during this research.



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41548410_0047

INTRODUCTION

The appearance of two minima for hydrochloric, nitric, and sulphuric acids in the magneto-optic apparatus led Allison and Murphy¹ to postulate the existence of a second isotope of hydrogen of mass two. Birge and Menzel² were able to account for the discrepancy between the atomic weights of hydrogen as determined by chemical methods and by a mass spectrograph by the postulation of an isotope of hydrogen of mass two in an abundance of about 1 part of H² in 4500 parts of H¹.

Urey, Brickwidde and Murphy³, obtained spectroscopic evidence for the existence of deuterium in a sample of hydrogen obtained by the fractionation of liquid hydrogen near its triple point. They obtained a concentration of about 1 part of deuterium per 1000 of protium.

Washburn and Urey⁴ were able to concentrate deuterium by the electrolysis of water with sulphuric acid electrolyte and platinum electrodes. They obtained a mixture of several parts of deuterium per 100 parts of protium.

Lewis⁵ obtained practically pure deuterium oxide by means of the electrolytic method.

¹F. Allison and A. J. Murphy, J. Am. Chem. Soc., 52, 3801 (1930):

²R. T. Birge and D. H. Menzel, Phys. Review, 37, 1670 (1931).

³H. C. Urey, F. G. Brickwidde and G. M. Murphy, Phys. Review, 39, 164 (1931).

⁴E. W. Washburn and H. C. Urey, Proc. Nat. Acad. Sci., 18, 496 (1932).

⁵G. N. Lewis, J. Am. Chem. Soc., 55, 1297 (1933).

Hertz⁶ has separated the two isotopes by the diffusion of hydrogen gas through porous materials. The heavy fraction was spectroscopically pure deuterium.

The concentration of the deuterium oxide in a mixture of the hydrogen oxides by electrolysis, as some of the hydrogen and oxygen are liberated, proceeds according to the Rayleigh⁷ diffusion separation formula given here as modified by Urey:⁸

$$\left(\frac{1-N_0}{1-N} \right)^{\frac{1}{\alpha-1}} \left(\frac{N_0}{N} \right)^{\frac{\alpha}{\alpha-1}} = \frac{W}{W_0}$$

where N_0 and N are the mole fractions of the deuterium oxide in the initial water and final residue, respectively, W_0 and W are the initial and final volumes, and α is the fractionation ratio.

In the work reported here an apparatus was constructed to concentrate deuterium oxide by the electrolytic method. The variation of the coefficient of separation with the temperature was determined for the electrolytic method.

A study was made of the fractionation of hydrogen by the solution of various metals in hydrochloric acid of a known deuterium content to which a small amount of foreign metal salt had been added.

APPARATUS AND PROCEDURE

The apparatus used for the separation of the isotopes of

⁶G. Hertz, Naturwissenschaften, 21, 884-5 (1933).

⁷Lord Rayleigh, Phil. Mag., 5 42, 493 (1896).

⁸H. C. Urey, Science, 78, 567 (1933).

hydrogen by Washburn,⁹ Lewis,¹⁰ and Taylor¹¹ is very simple and consists of two metal electrodes immersed in an electrolyte contained in a glass hydrometer jar and cooled by placing the glass jar in a bath of running water.

The method has certain disadvantages which are overcome in the apparatus described. The temperature of the operating cell remains lower due to the more rapid transfer of heat through the metal wall than through the glass wall. Larger amounts of current can be passed through the cell per unit volume of electrolyte as the cylindrical shape of the electrode exposes a larger amount of surface per unit volume of electrolyte.

The large unit (Fig. 1) consists of two concentric tubes, the smaller, 5.0 cm. in diameter, of nickel and the larger, 10.6 cm. in diameter, of iron. The portion IJ holds about 3.5 liters of alkaline solution.

The two tubes are insulated from each other by heavy rubber washers, H, Q and K. The washer K is cemented to the metal on which it rests. The screws which hold the apparatus together are insulated on one side by the bakelite insulators D. The solution is introduced or removed at R, and an outlet for gases is at B. Electrical connections are made at A, anode, and E, cathode. The tube P is filled with water for cooling which is admitted at M. With 140 amperes operating current the water which escapes from N has a temperature only 0.4° above that which enters at M. The apparatus is made gas tight, except for the opening at B, by the packing C, pressed in by the screw T.

⁹E. W. Washburn and H. C. Urey, op. cit.

¹⁰G. N. Lewis and R. T. Macdonald, J. Chem. Phys., 1, 341 (1933).

¹¹H. S. Taylor, H. Eyring and A. A. Frost, J. Chem. Phys., 1, 823 (1933).

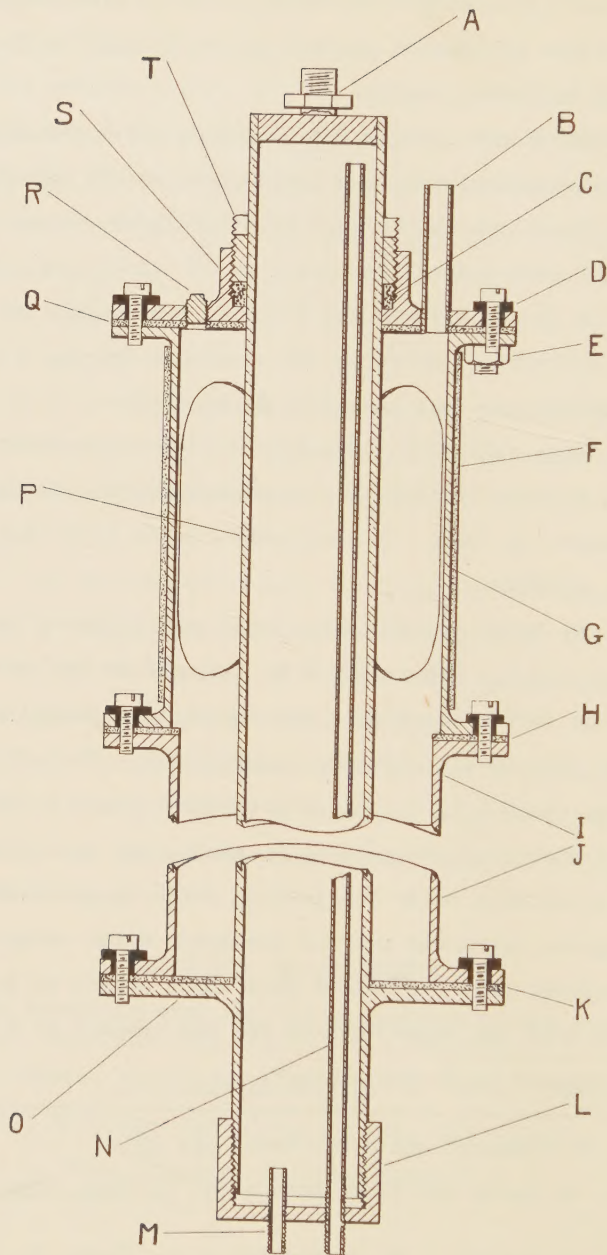


Fig. 1.

The upper length of 10 cm. tubing, G, 15 cm. in length, is covered with rubber F from the inner tube of an automobile tire, and most of the wall of the steel tube is cut away. The purpose of the rubber is to avoid danger in any accidental explosion of the gas. The joint H is for convenience of construction. The flange O is welded to the pipe, P. The cap L is screwed on to the pipe P.

The second type of unit is shown in Fig. 2.

The vessel E is a glass hydrometer jar 7.5 cm. wide, and 37.5 cm. tall. The cathode J consists of a pipe 3.0 cm. in diameter and 37.5 cm. long, welded shut at one end and capped at the other, with a binding post B and connections A and K for the water used for cooling. The cathode is supported and insulated by the rubber stopper D and centered at the bottom of the cell with the glass flange G. The anode is a 22 B and S gauge nickel sheet 20 cm. wide and 30 cm. long. A strip of the sheet extends through the rubber stopper and has the binding post H attached to it. The nickel sheet is of cylindrical form to fit the inside of the glass jar. The filling tube C extends to the bottom of the cell and serves, also, to facilitate emptying the cell. The cell has a volume of 800 cc. of alkaline solution and is gas tight, except for the gas outlet I.

These cells operate at 21° C. when the operating current is 45 amperes and the initial temperature of the cooling water is 16°C.

A smaller set of 10 cells of similar construction with a capacity of 250 cc. of solution and 25 amperes of operating current were made. The hydrometer jar is 5 cm. in diameter and 30 cm. tall. The nickel electrode is 12.5 cm. wide and 25 cm. long. The iron electrode is 30 cm. long and 2.0 cm. in diameter. The

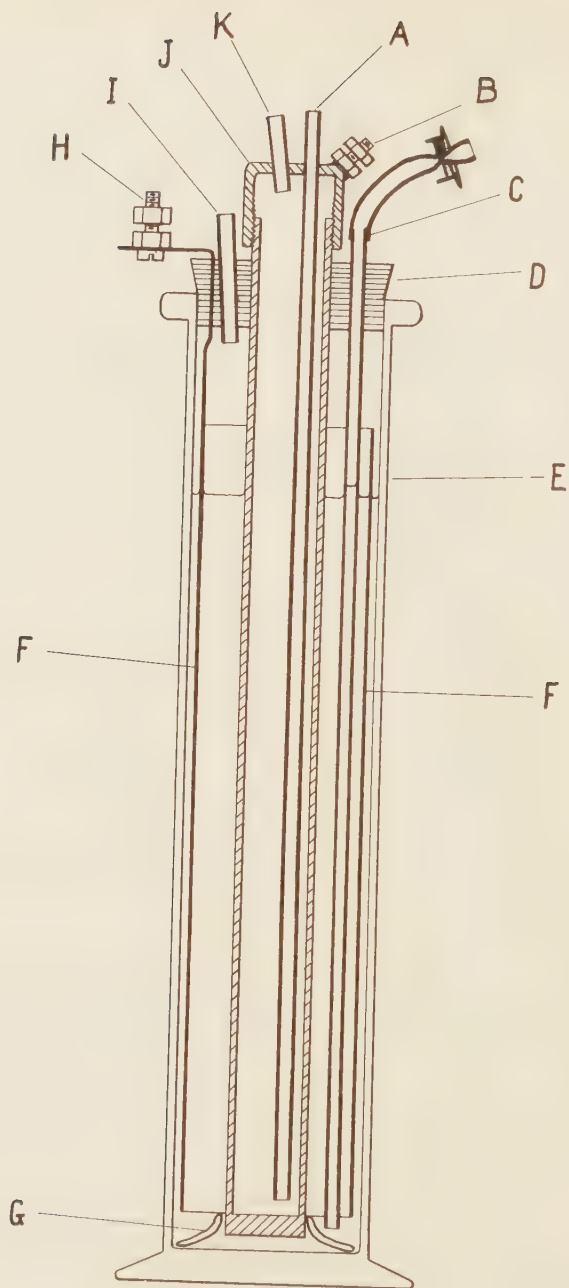


Fig.2

rest of the apparatus is proportional in size.

The gas outlets of the ten small cells are connected, each through an individual sand trap to a burning apparatus as shown in Fig. 3.

The gaseous mixture of hydrogen and oxygen enters at A, bubbles through a mercury bubbler L, passes through a 10 cm. sand trap B packed with asbestos at each end to keep the sand in place, is ignited by the heated platinum wire, F, and burns from the nozzle E. The rubber stopper C supports the capillary tubing with a 1.5 mm. nozzle and the leads from the transformer, J, which heat the platinum filament. In the condenser, G, the combustion chamber is 4 cm. in diameter and 25 cm. long. The cooling water enters at I and is discharged at D. The water formed by recombination of the gases passes through H into the container M where it is protected from the atmosphere.

The pressure release K affords a means of escape for the gases should the capillary tube become blocked.

The ten large metal cells are connected in series. Two banks of nineteen each of the large glass cells are connected in parallel. The ten small cells are arranged into two sets of five cells each connected in parallel and they in turn are joined in series to fifteen of the large glass cells. This bank of twenty-five cells is connected in parallel to the two banks of nineteen cells each and the three banks in parallel are connected in series to the ten large cells.

This arrangement of seventy-three cells is connected to a 110 volt direct current generator and has an operating current of 135 amperes.

The apparatus electrolyses 26 liters of water per day at full load. Two liters of this water is recombined by the burning cells.

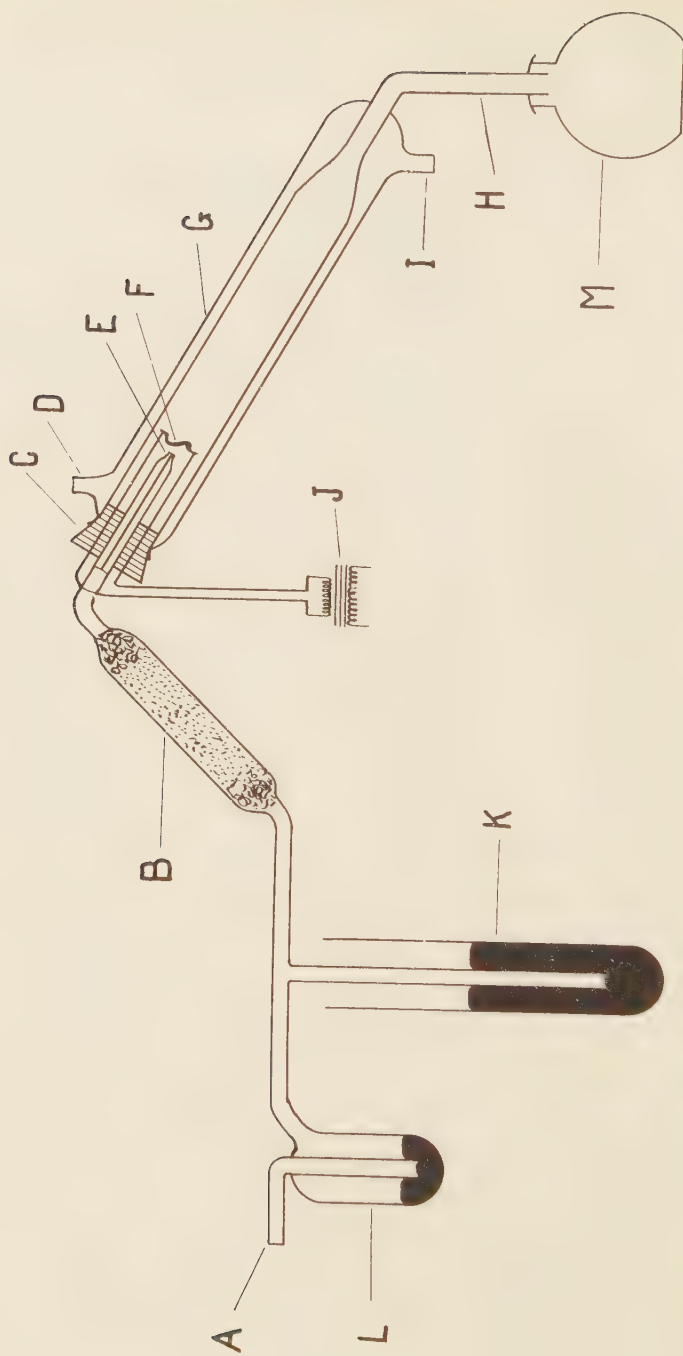


Fig. 3

OPERATION OF APPARATUS

The water for charging the cells initially is electrolyte from commercial hydrogenation cells which has a concentration of deuteriohydrogen of 65 parts per million more than ordinary water. All of the water is distilled from an iron still to remove the old caustic, carbonate and other impurities present. The distilled water is made 0.5 molal by the addition of pure solid sodium hydroxide. The cells are filled and the solution is electrolyzed to one-third of the initial volume. The residues from two of the cells are added to a third cell. The two empty cells are filled with the initial electrolyte and the electrolysis carried on to one-third of the initial volume. The water from the cell which has been reduced to one-ninth of the volume of the initial water (cut = 9) is removed. This water is filtered through a pyrex sinter glass filter to remove any sediment which may have been formed. This operation can usually be omitted. The 9 cut water is distilled until only one-fourth of the water remains as residue. This residual alkali is used to make the initial water and the 9 cut water 0.5 molal with respect to sodium hydroxide. In this manner no fresh alkali need be added to the system and loss due to interchange is avoided.

The gases from the electrolysis of the 9 cut water are recombined by combustion in the apparatus previously described. This recombined water is as rich in deuteriohydrogen as the initial water and is added to it.

After each cut of 9, part of the water is distilled off and the alkali concentration is adjusted. The water from the

various recombinations is added to the proper stage of the electrolysis.

Table I shows the concentration of deutohydrogen oxide with each stage of electrolysis. W_0 and W are the initial and final volumes and N is the mol fraction of $H_2^{18}O$. These results assume Lewis' value of 1.1056 grams per cc. as the density of pure $H_2^{18}O$ and the value of 20 parts per million as the concentration of deutohydrogen oxide in ordinary water. It is also assumed that the value of α does not change with concentration.

TABLE I

Mole Fraction	W_0/W
0.00075	1
0.00414	9
0.023	81
0.127	729
0.702	6561
0.90	.13000

DENSITY DETERMINATIONS

The concentrations of deutohydrogen oxide in water were determined by density measurements of the water.

The samples of water for density determination are carefully distilled from alkaline permanganate to remove any organic materials present.

The pycnometer used is spherical in shape and has a volume of 30 cc. The pycnometer is filled through an 0.8 mm. diameter capillary tubing with a Luer syringe. The top of the capillary is fitted with a ground glass stopper. After the pycnometer is filled it is placed under a bell jar and carefully evacuated to

remove any dissolved gases. The pycnometer is placed in a thermostat at $20.0^{\circ}\text{C.} \pm 0.001$ and the height carefully adjusted to the etched mark on the neck. The adjustment is made by a fine thread and any deviation is noted by a telescope. The error in adjusting the height of the meniscus is ± 0.01 cm.

The pycnometer was weighed on a high sensitivity analytical balance.

The determinations were all made in duplicate using similar pycnometers. The deviation from the mean for each pair of determinations was 2 parts per million.

VARIATION OF α WITH TEMPERATURE

The value of α is known to vary with the composition of the electrodes which are used in the electrolysis.¹² Bell¹³ predicted that the efficiency of separation should decrease about 35% for a temperature rise from 0° to 100° C. A knowledge of the actual variation is desirable for the most efficient separation.

An apparatus was constructed using two smooth nickel electrodes 3 cm. wide and having 21 cm. immersed initially in the solution. The cell was filled with 250 cc. of 0.5 M KOH of known deutohydrogen oxide content. The operating current was 15 amperes. The gases were passed through an efficient reflux condenser and recombined as previously described. The temperature was determined by a thermometer immersed in the cell, the bulb adjusted to a height of five centimeters from the bottom between the electrodes. The results are shown in Table II and in Fig. 4.

¹²B. Topley and H. Eyring, J. Chem. Phys., 2, 217 (1934).

¹³R. P. Bell, J. Chem. Phys., 2, 164 (1934).

TABLE II*

T	W_0	W	N	α
10	250	130	0.00868	6.75
20	250	130	0.00859	6.02
35	250	130	0.00853	5.72
65	250	57.5	0.01600	4.85
90	250	60	0.01440	4.03
98	125	25	0.01635	3.91

* N_0 0.000497 Initial mole fraction deuterohydrogen.
T Temperature Centigrade.
 W_0 Initial volume.
W Final volume.
N Mole fraction in residue.
 α Separation coefficient.

THE FRACTIONATION BY CHEMICAL METHODS

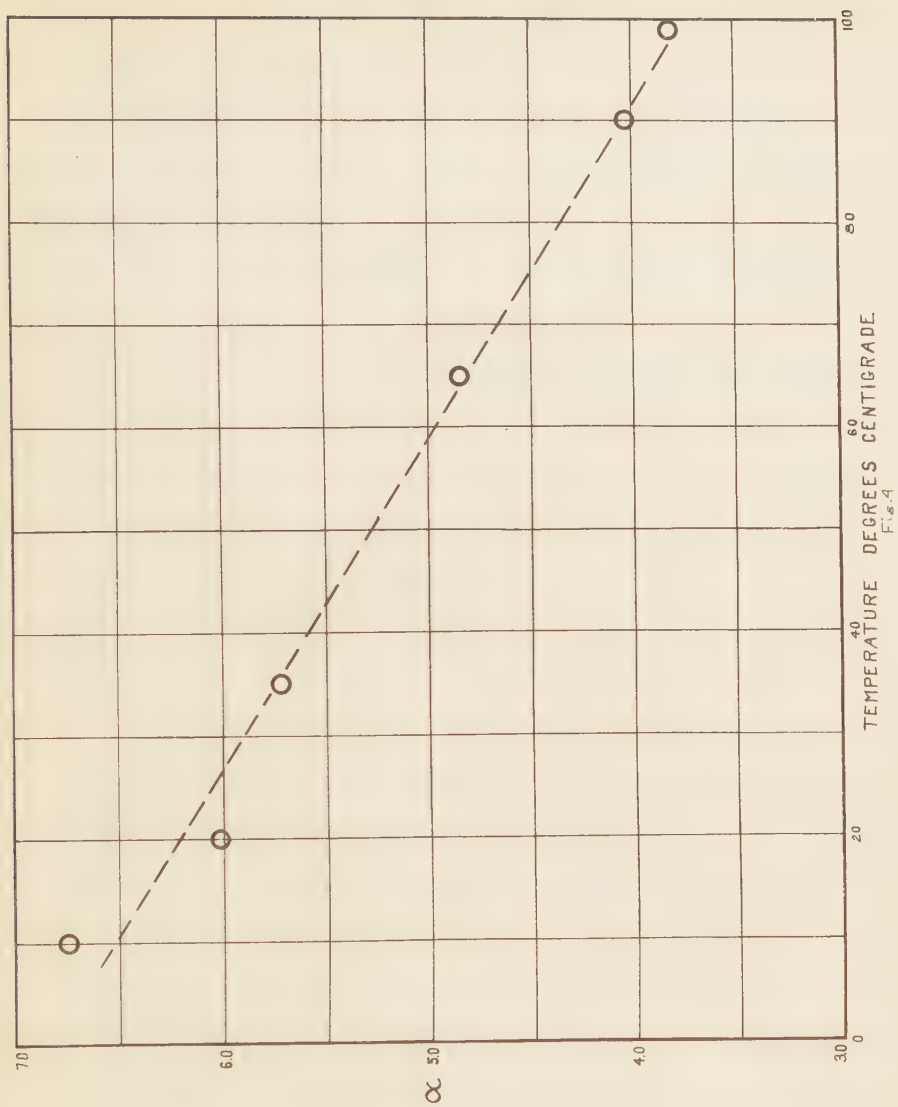
The isotopic fractionation of hydrogen by displacement from acid, alkali, or water by the addition of metals has been studied by Hughes, Ingold, and Wilson.¹⁴ Their results indicate that the value of α varies greatly with the purity of the metal which displaces the hydrogen. Since the displacement is a surface phenomenon, the value of α would be expected to vary as the condition of the surface is varied.

If, as the reaction proceeds, a metal is deposited from solution upon the metal liberating the hydrogen, the value of α should be different from that obtained for the pure metal.

The liberation of hydrogen from hydrochloric acid by zinc was employed in this series of experiments.

Water of a known deuterohydrogen oxide content was allowed

¹⁴E. D. Hughes, C. K. Ingold and C. L. Wilson, J. Chem. Soc., 493, April, 1934.



to dissolve a weighed amount of dry hydrogen chloride gas. The hydrogen chloride gas was prepared by introducing concentrated aqueous hydrochloric acid at the bottom of a flask containing concentrated sulphuric acid. The liberated gas was passed through a sulphuric acid wash bottle, dried in a P_2O_5 tower and dissolved into a weighed quantity of water. The resulting acid was 12.01 Molal.

A sample of the hydrochloric acid was carefully neutralized by the addition of sodium carbonate. The water was distilled from the sodium chloride formed and the concentration of deutohydrogen determined by density agreed with the concentration of deutohydrogen calculated from the concentration of the initial water and the amount of HCl gas absorbed to one part per million.

Fifty grams of mossy zinc were introduced into a three necked flask. A thermometer was introduced into one neck, and a dropping funnel containing the hydrochloric acid was placed in the neck opposite the thermometer. The hydrogen was liberated through the central neck and the vapors were condensed by an efficient reflux condenser. The gas was burned in the recombination apparatus. The necessary oxygen was supplied by passing previously dried air of the proper amount into the chamber just behind the capillary nozzle.

The hydrochloric acid, or the hydrochloric acid salt solution was introduced regularly enough to keep gas evolving steadily.

Any unreacted hydrogen chloride was neutralized to NaCl by the addition of sodium carbonate. The remaining water was distilled from the solution and the residue heated to $350^{\circ}C.$ to drive off all of the water.

The results are given in Table III.

TABLE III

Metal	Added Metal Salt	N	α	T
Zn	-	0.00489	2.5	40
Zn	Tin (stannous)	0.00486	1.6	75
Zn	Pt	0.00510	5.1	40
Zn	Pb	0.00512	6.5	40
Zn	Hg	0.00464	1.5	75
Zn	Fe	0.00488	2.4	40
Zn	Co	0.00503	3.9	40
Zn	Ni	0.00513	6.5	40
Sn	-	0.00440	1.1	75
Sn	Pt	0.00450	1.2	75

The initial mole fraction N_0 of deutohydrogen was 0.00437. The ratio of the volumes W/W_0 for the reaction was 0.829. Column 1 gives the metal present to liberate the hydrogen. Column 2 gives the metal salt 0.001 mole of which is dissolved in the 100.0 cc. of hydrochloric acid. Column 3 gives the values of N, the mole fraction of deutohydrogen oxide in the residue water. Column 4 contains the value of α as calculated from the Rayleigh equation. The value is correct to 0.2 units. The last column gives the highest temperature to which the reaction mixture was heated.

The value of α for Zn is much lower than that reported by Hughes, Ingold, and Wilson¹⁵ but the value of α for Zn, Pb is nearly equal to their value. The increase of α with the increase in catalytic hydrogenation activity in the sequence Fe, Co and Ni indicates a relationship between the two phenomena.

¹⁵Hughes, Ingold and Wilson, loc. cit.

The small amount of mercury and tin salts added decreased the rate of gas evolution very markedly as compared to pure Zn, while the addition of the cobalt, lead, and nickel salts increased the rate of reaction.

SUMMARY

1. An apparatus is described for the separation of deuterium oxide from protium oxide by electrolysis of aqueous alkaline solution. Deuterium oxide of greater than 95% purity has been obtained.

2. The variation of α with temperature has been determined for nickel electrodes in alkaline solution. The variation is much greater than that predicted by theory.

3. The fractionation of hydrogen by the reaction of pure metals on hydrochloric acid and hydrochloric acid with known impurities was studied. The value of α was very much dependent on the nature of the impurity added.

